

# **THERMOPLASTIC INFUSIBLE RESIN SYSTEMS: CANDIDATES FOR THE MARINE SECTOR?**

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## **Abstract**

This work investigated the feasibility of the use of a novel infusible thermoplastic resin (Elium 150 from Arkema) for composite laminate manufacture by resin infusion methods and possible application in the shipbuilding sector. We compared the properties of Elium glass-fibre laminates with those of laminates infused with state-of-the-art thermosetting epoxy and urethane acrylate resins. The Elium laminates matched the mechanical performance (flexure and interlaminar shear strength) of the epoxy and surpassed that of the urethane acrylate counterpart. However, the mechanical performance of the Elium laminates after immersion in water at 35 °C for 28 days deteriorated compared to urethane acrylate, but was comparable in flexural properties to that of the epoxy. The combination of superior mechanical performance coupled with acceptable environmental resistance and comparable composite laminate manufacturing conditions makes the infusible thermoplastic a possible future candidate matrix over commercial thermosetting resin options.

## **1. Introduction**

Fibre-reinforced polymer (FRP) composite materials find increasing acceptance and application in a number of transport sectors (aviation, land & waterborne transport [1]) due to their lightweight nature which provides a significant advantage in terms of lower fuel consumption and greenhouse gas emissions, in line with relevant EU directives.

Particularly in waterborne transport and shipbuilding, FRP composites are currently dominating the manufacture of vessels up to 50 m in length, with liquid resin infusion (LRI) being the most frequently used manufacturing technique and vacuum-assisted resin transfer moulding (VARTM) in particular the most widely adopted LRI variant. The primary options for the reinforcement include glass and carbon fibres, whilst thermosetting resins are a traditional choice for the matrix.

Recent developments in the field have seen the introduction of novel, infusible thermoplastic resins into the market [2], with low viscosities and thus suitable for resin infusion processing. The use of a thermoplastic matrix has a number of potential advantages over a thermoset (performance, re-processable, recyclable). Moreover, when compared to thermosetting systems based on styrene as reactive diluent (e.g. polyester, vinylester, urethane acrylate), the novel infusible thermoplastic option provides a styrene-free offering with otherwise similar characteristics (e.g. resin viscosity, time to gel point), yet with distinct environmental benefits.

In this work we conducted an extensive, direct comparison of FRP composite laminates manufactured by VARTM with a novel infusible acrylic thermoplastic (Elium 150 from Arkema), and state-of-the-art thermosetting resins. Our comparison included manufacturing aspects (infusion time,

recommended curing and post-curing schedule) as well as laminate quality, and mechanical and thermomechanical performance in both dry and wet (after immersion in water) conditions.

## 2. Materials and Methods

### 2.1. Manufacturing of Composite Laminates by VARTM

Composite laminates (350 x 500 mm) were manufactured on glass or aluminium tools at room temperature. Unidirectional non-crimp glass fabric (Saertex UD NCF 996 gsm with PPG Hybon 2002 E-glass fibre) was the reinforcement of choice along with two thermosetting resins (urethane acrylate Crestapol 1210 from Scott Bader and epoxy Prime 27 from Gurit) and an infusible thermoplastic (Elium 150 from Arkema). The recommended ratios of hardener/catalyst/accelerator (as appropriate) from the supplier were used for each system. Four (4) plies of glass fabric were cut in the above mentioned dimensions and placed on the tool in a symmetric/unidirectional stacking sequence  $[0^\circ]_{2S}$  with a glass preform mass of approximately 650 g targeting a nominal laminate thickness of 3 mm. The infusion time was measured from the opening of the resin inlet to the closure of the outlet (outlet was closed on observing bubble-free resin in the outlet tube).

### 2.2. Mechanical testing

#### 2.2.1. Interlaminar shear strength (ILSS)

Interlaminar shear strength tests were conducted according to ISO 14130. Five (5) samples of 30 x 15 x 3 mm were used for each laminate to determine the apparent inter-laminar shear strength (ILSS).

#### 2.2.2. 3-point bending

Flexure tests were conducted according to ISO 14125. Five (5) samples of 80 x 15 x 3 mm were used for each laminate to determine the flexural strength and flexural modulus for each case.

### 2.3. Dynamic Mechanical Analysis

Dynamic Mechanical Analysis was performed in a TA Instruments (USA) Q800 Dynamic Mechanical Analyser in 3-point bend testing mode, with a displacement amplitude of 10  $\mu\text{m}$  and frequency of 1 Hz. Laminate specimens with nominal dimensions of L x W x T equal to 50 x 12 x 3 mm were used. The specimens were heated from ambient temperature to an appropriate end temperature based on their expected  $T_g$  at a rate of 5°C/min. Storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan \delta$  were recorded.

### 2.4. Scanning Electron Microscopy

Cross-sections of the composite laminates were examined using a Hitachi SU-70 Analytical Field Emission SEM, at accelerating voltage of 10 kV and working distance of 10 mm. Specimens were examined as received, and after manual polishing (using P800 and P1000 SiC paper). The samples were sputter-coated with gold for 30 seconds using an Emitech K550 sputter coater before SEM observation.

### 2.5. Density

Specific gravity was calculated by the displacement method according to ASTM D792-08, using five (5) samples for each laminate with dimensions 25 x 12 x 3 mm.

### 2.6. Fibre volume fraction ( $V_f$ )

Fibre volume fractions were determined by a resin burn-off test according to ISO 1172, using five (5) samples for each laminate.

## 2.6. Water immersion studies

Laminate specimens for ILSS and flexure were immersed in distilled water in a water bath at 35 °C for 28 days, and tested after removal. Three samples were used for each laminate in each test (with the exception of Prime 27, for which two ILSS specimens were measured due to equipment issues).

## 3. Results and Discussion

The comparison of the composite laminates in this study was conducted across a number of aspects, namely manufacturability for resin infusion (resin/curing agent formulation, viscosity, infusion temperature and time, curing and post curing requirements), quality of produced laminates (achieved fibre volume fraction and  $T_g$ ), mechanical properties as-manufactured and effect of water immersion on mechanical properties.

The manufacturing details for the three laminates are presented in Table 1. It is evident that the infusible thermoplastic is quite similar in terms of viscosity and infusion time at room temperature to its thermosetting counterparts. It also doesn't require any post-curing according to the resin manufacturer; it can be left to cure at room temperature on the tool overnight, and is subsequently easily demoulded. This is a particularly attractive feature for complex shapes with curvature, which are quite abundant in shipbuilding.

**Table 1.** VARTM manufacturing details for composite laminates

Resin Details	Resin:Curing agent(s) (w/w)	Viscosity <sup>a</sup> (cP)	Tool	Infusion time/T (min/°C)	Curing schedule	Post-curing schedule
Urethane Acrylate CRESTAPOL 1210	100:2:1:1 <sup>b</sup>	175 cP at 25 °C (neat resin)	Glass	11/21.1	1h at RT 1h at 45 °C	None required
Epoxy PRIME 27	100:28 (Prime 27 slow hardener)	285 cP at 20 °C (mixture)	Glass	13/18.8	Overnight at RT	7h at 65 °C
Acrylic thermoplastic ELIUM 150	100:2.5 (benzoylperoxide Luperox A40FP-EZ9)	100 cP at 25 °C (neat resin)	Glass	23/21.9	Overnight at RT	None required

<sup>a</sup>: values from TDS; <sup>b</sup>: 2 parts by weight of Accelerator D (10% solution of dimethylaniline in styrene) : 1 part by weight of Accelerator G (1% cobalt solution in styrene) : 1 part by weight of peroxide catalyst (Trigonox 44B)

All three laminates were shown to reach the expected  $T_g$  levels when tested by DMA [3-5], indicating a complete cure cycle. Elium 150 is expected to show a heat deflection temperature of 109 °C, and indeed showed an onset transition in the storage modulus at 96 °C and a peak in the loss modulus at 107 °C (Figure 1).

Mechanical properties of the as-manufactured composite laminates are summarized in Table 2. The achieved fibre volume fractions for all three resins were in the region of 56-58% (using the same UD glass fabric), indicating again that the infusible thermoplastic behaves in terms of manufacturing very similar to a thermosetting resin. Elium 150 clearly exceeded the urethane acrylate (Crestapol 1210) thermoset in both interlaminar shear and flexural strength values. Compared to the standard epoxy (Prime 27), Elium showed higher flexural and slightly lower interlaminar shear strength values. Overall, it is quite clear that Elium 150 is comparable in its performance to the epoxy laminate and outperforms the laminate made from a styrene-based resin in the dry condition.

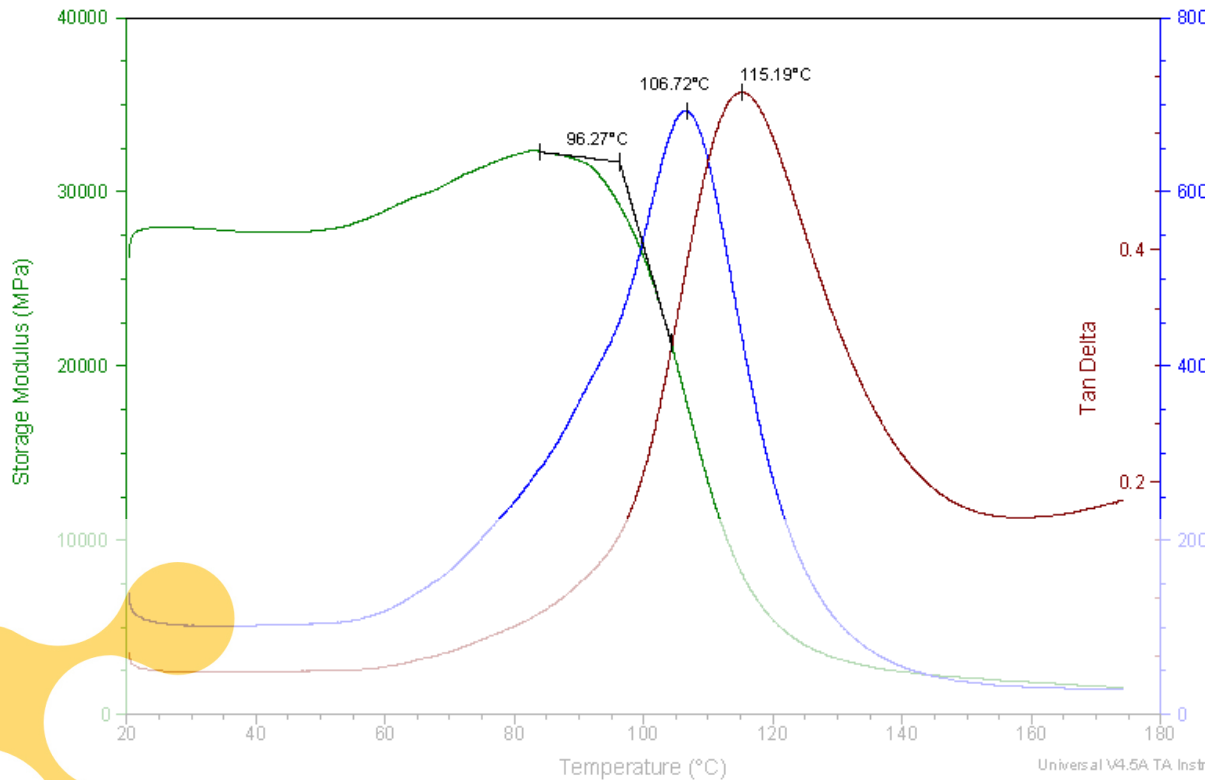


Figure 1. Dynamic mechanical analysis profile of the Elium 150/glass laminate

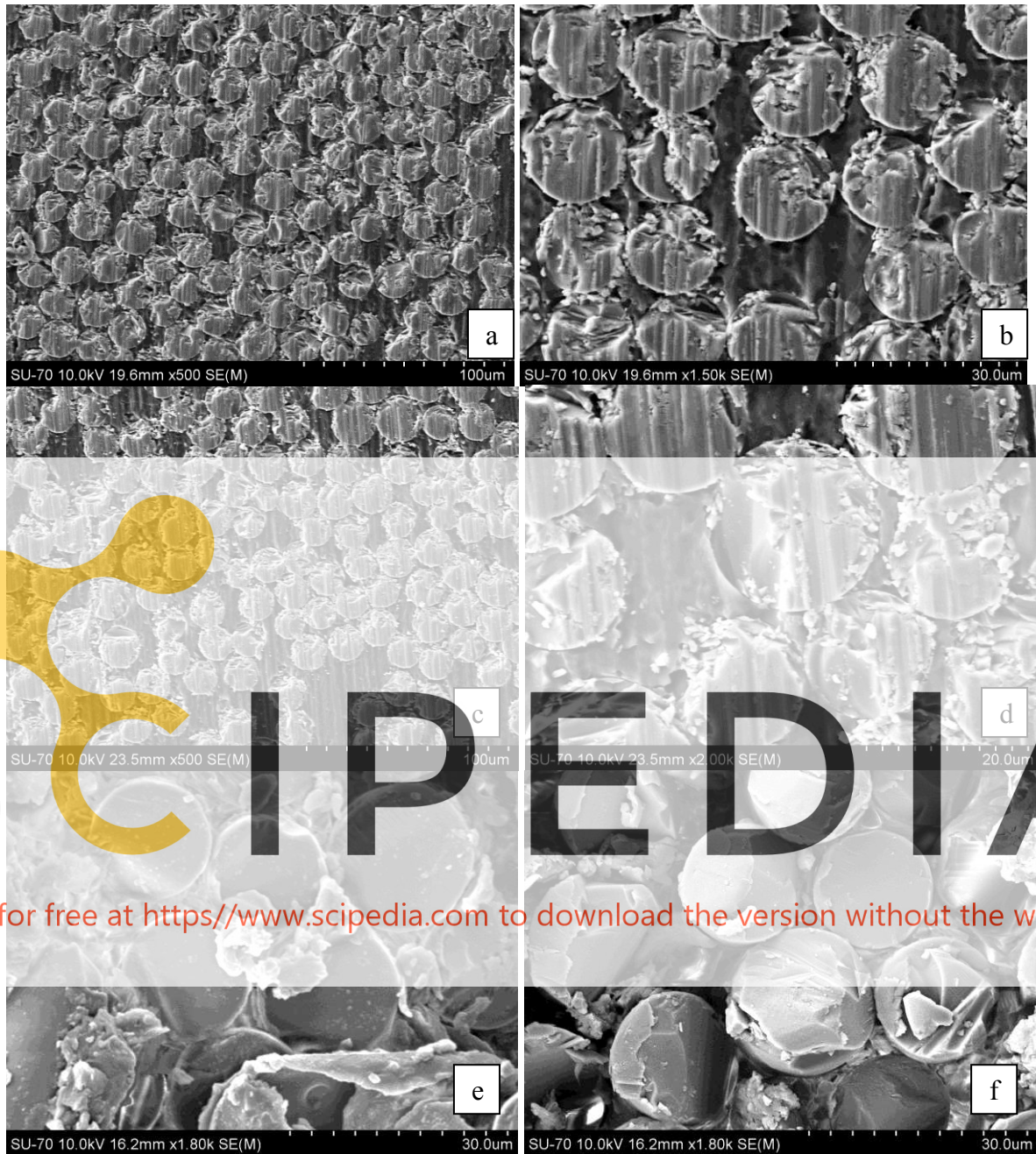
Table 2. Mechanical (ILSS, flexure) and physical ( $V_f$ , density) properties of composite laminates in the Dry Condition

Resin Details	$V_f$ (%)	Density (g/cm <sup>3</sup> )	Apparent Inter-Laminar Shear Strength (MPa)*	Flexural Strength (MPa)	Flexural Modulus (GPa)
Urethane Acrylate CRESTAPOL 1210	57 (±0.3%)	2.017 (±0.7%)	42.09 (±3.0%)	790.61 (±11.3%)	34.52 (±2.0%)
Epoxy PRIME 27	58 (±0.9%)	2.061 (±0.5%)	58.04 (±2.4%)	917.1 (±2.4%)	35.37 (±2.8%)
Acrylic thermoplastic ELIUM 150	56 (±1.0%)	1.999 (±0.4%)	56.87 (±3.6%)	942.8 (±3.8%)	33.86 (±1.6%)

\*Minimum required laminate property values in accordance with [6]: ILSS at least 15 MPa; Flexural Strength and Flexural Modulus for a laminate with equivalent fibre mass fraction (0.72) at least 367 MPa and 19.5 GPa, respectively

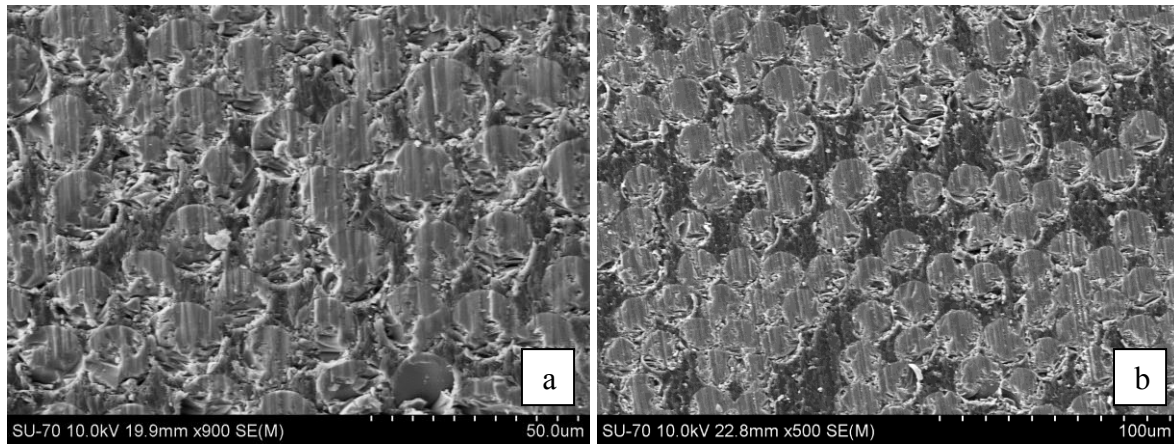
Scanning Electron Microscopy on cross-sections from the as-manufactured laminates provided information on the infusion quality/void content and the matrix/fibre interface. All laminates showed generally good fibre impregnation (a selection of SEM images in Figures 2a, 2b, 3a), as expected from their good mechanical properties (Table 2).





**Figure 2.** SEM images of the Elium 150/glass laminate cross-sections: as-manufactured (a, b; polished; Table 2) and after immersion in water for 28 days at 35 °C (c, d: polished; e, f: unpolished; Table 3). Longitudinal lines in the polished samples come from the polishing action/direction.

The effect of prolonged water immersion on the mechanical properties of the three laminates is detailed in Table 3. Water absorption less than 70 mg (after 7 days of immersion), and a drop in mechanical properties no greater than 25% after 28 days are the main requirements for material qualification in shipbuilding [6].



**Figure 3.** SEM images of the Prime 27/glass laminate polished cross-sections (a: as-manufactured; b: after immersion in water for 28 days at 35 °C). Longitudinal lines come from the polishing action/direction.

Elium 150 appeared to absorb similar amounts of water to the epoxy. The urethane acrylate laminate recorded the lowest water uptake and the smallest drop in all mechanical properties. The Elium laminate showed the sharpest drop in ILSS value (37.5%) compared to the dry state value. In terms of flexural strength, Elium and Prime 27 were almost identical, with a drop of 17-18%. Flexural modulus was less affected for Elium. As in Table 1, Elium appears overall comparable with the state-of-the-art epoxy in terms of environmental resistance, with the exception of the ILSS values (yet with a high coefficient of variation); the latter may suggest a more affected matrix and/or Elium/glass interface due to water ingress (possibly also due to hydrolysis of the acrylic-based Elium matrix).

**Table 3.** Comparison of mechanical properties (Table 1) after immersion in water (35 °C, 28 days)

Resin Details	Apparent Inter Laminar Shear Strength (MPa)	Change compared to dry state (%) (Table 1)	Average mass uptake ILSS specimens (mg) (±30%)	Flexural Strength (MPa) (±1.5%)	Change compared to dry state (%) (Table 1)	Flexural Modulus (GPa) (±2.3%)	Change compared to dry state (%) (Table 1)	Average mass uptake flexure specimens (mg) (±16%)
Urethane Acrylate CRESTAPOL 1210	41.90 (±2.4%)	-0.5	4.6 (±30%)	785.9 (±1.5%)	-0.6	35.34 (±2.3%)	+2.4	21.0 (±16%)
Epoxy PRIME 27	48.45 (±2.9%)	-16.5	16.1 (±7%)	746.7 (±5.0%)	-18.6	33.80 (±6.1%)	-4.4	39.9 (±2%)
Acrylic thermoplastic ELIUM 150	35.56 (±14.5%)	-37.5	9.7 (±2%)	779.8 (±11.6%)	-17.3	33.99 (±1.0%)	-0.4	34.7 (±4%)

For this reason, SEM was also conducted on laminate specimens after water immersion (Figures 2c, 2d, 2e, 2f, 3b) and compared to images obtained for the as-manufactured laminates. Crestapol 1210 (not shown here) showed very little difference in terms of SEM imaging in the dry and wet condition, in line with its minimal change in mechanical properties.

In the case of Elium 150 (Figure 2), SEM suggested the presence of some localised resin-poor areas in the wet samples, potentially linked to possible hydrolysis of the acrylic matrix. Otherwise, there was again little visible difference overall by SEM between dry and wet samples, which can be partly

attributed to the overall low average mass uptake (Table 3) for all samples. Nevertheless, the effect on mechanical properties was significant for Prime 27 and Elium 150, as shown in Table 3.

#### 4. Conclusions

This study highlighted the suitability of the novel infusible acrylic thermoplastic option for FRP laminate manufacture by liquid resin infusion in a shipbuilding environment. The laminates produced by the infusible thermoplastic were of high quality, and comfortably exceeded the minimum requirements set by classification societies [6] in ILSS and flexural properties (see note in Table 2). Elium 150 matched the mechanical performance of a state-of-the-art epoxy resin (Prime 27), and outperformed laminates produced with resins based on styrene reactive diluent technology (urethane acrylate Crestapol 1210 in this study).

The drop observed in flexural properties for the thermoplastic laminates after immersion in water was comparable to that of the epoxy-based laminates and within the allowed 25% reduction compared to the dry state [6]. The reduction in ILSS values for Elium 150 (> 25%) observed in this study could be improved by e.g. employing the allowed post-curing schedule according to [6] (16 h at 40 °C), or selecting a glass fibre fabric with bespoke sizing for the Elium resin range.

The new infusible acrylic thermoplastic combines good manufacturability in a liquid resin infusion context with epoxy-like laminate properties, and additionally offers a re-processable, styrene-free resin option to the shipbuilding industry. Once a competitive price range could be established for the Elium range, it would be expected that its acceptance and adoption by the shipbuilding industry would increase accordingly.

#### Acknowledgments

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